

**SELF-EXFOLIATED  
TRIAZOLE-TRIFORMYL  
PHLOROGLUCINOL BASED COVALENT  
ORGANIC NANOSHEETS FOR HIGH AND  
REVERSIBLE LITHIUM ION STORAGE**

**RELATED APPLICATIONS**

**[0001]** This application is a continuation of International Patent Application No. PCT/IN2018/050351, filed May 31, 2018, and published as International Patent Publication No. WO 2018/220650 on Dec. 6, 2018, which claims priority to Indian Patent Application 201721019419, filed Jun. 2, 2017. Each of these prior patent documents is incorporated by reference herein in its entirety.

**FIELD OF INVENTION**

**[0002]** The present invention relates to covalent organic nanosheets (CONs), methods of making such nanosheets, and devices comprising such nanosheets. More particularly, the invention relates to covalent organic nanosheets (CONs) made of triazole based diamine and triformyl phloroglucinol. The 2D structure of these nanosheets enables their facile amalgamation as an anodic material in a coin cell battery, which exhibits exceptionally high specific capacity of ~720 mAh/g at a current density of 100 mA/g.

**BACKGROUND AND PRIOR ART**

**[0003]** Covalent organic frameworks (COFs) owing to their modular structure and ordered porosity can serve as chemically tunable supports. Typically Lithium ion batteries (LIB) are built from Graphite and LiCoO<sub>2</sub>. A common feature of these anodic and cathodic materials is their 2D structure. Since their initial discovery, many 2D materials with comparable layered structure have been explored as Li insertion/de-insertion substrate.

**[0004]** Some of the highly desirable characteristics of a superior electrode material include their moderate to high surface area to ensure maximum charge storage per unit area, and the other is the hierarchical porosity rendering facile access for favourable kinetics. One of the key attributes of graphite which has made it historically most utilized storage material is its ability to exfoliate. Exfoliation-assisted surface area/porosity enhancement and adsorption site creation is facile in organic substrates such as graphene, MoS<sub>2</sub>, CNT or other carbonaceous structures, which makes them components of top-performing Li and Na storage materials for batteries. In this regard, Covalent Organic Frameworks could have much more to offer as they are typically built with pre-designed cross-linking units to assist construction of extended/periodic hexagonal or square-grid layers. Also, their C/N or C/B, or in general, the atom1/atom2 ratio can be controlled with stoichiometric exactness and the chemical function (e.g. Nitrogen: pyridyl vs. triazine vs. Schiff) which can be modified.

**[0005]** Another feature of relevance for developing as electrode material comes from the type of inter-layer interactions they possess. Typically, the COF layers are held together by interlayer  $\pi$ - $\pi$  interactions or in special cases via additional hydrogen bonding. In their optimized structure, the interlayer separations typically fall in the range of 3.2 to 4.5 Å. Moreover, unlike graphite, the layers of COF are not built from fused aromatic rings. Hence, the interaction forces are optimal for holding them together, but more

importantly to support facile exfoliation without losing the overall structure. Particularly, the COFs formed by imine linkages are amenable to exfoliate into nanosheets. This exfoliation can have marked consequence in ion storage (S. Wang, Lijiang Wang, Kai Zhang, Zhiqiang Zhu, Zhanliang Tao, and Jun Chen, Nano Lett., 2013, 13, 4404-4409. (b) Oscar A. Vargas C., Álvaro Caballero and Julian Morales, Nanoscale, 2012, 4, 2083-2092).

**[0006]** Also, in COFs, the building units are longer and contain flexible bonds. Therefore the layers of COF show a by demand structural rearrangement which facilitates accommodating the extra-framework species, be it ions or nanoparticles. This flexibility and tunability has made COFs find its use in gas storage, hydrogen evolution, proton conduction, quantum sieving, photoconductivity, catalysis, and even in self-cleaning superhydrophobic surfaces and sensing. Conducting and semi-conducting COFs built from components rich in electronic character (conjugated  $\pi$ -clouds, donor-acceptor nodes or high polarizing moieties) have been used as electrodes or electrolytes.

**[0007]** The research on lithium storage using several carbon rich materials, polymers and classical inorganic oxides, sulfides have been known for several decades. Lithium insertion in Nitrogen-doped graphenes is also known. In comparison, less is known about utilizing covalent organic frameworks for lithium ion storage. As an effective approach, Yuliang Li et al. designed a porphyrin-thiophene-based conjugated COF with enhanced intrinsic electronic conductivity and demonstrated high specific capacity of up to 666 mAh/g, but this specific capacity was seen to drop significantly with increasing current density. Also, there are some interesting theoretical studies focused on the inclusion of Li into the frameworks of COFs, all of which point at the Li ions being bound to the hydrocarbon backbone, more precisely, to the aromatic rings forming the COF that can facilitate chemical interactions with Li.

**[0008]** Similarly, Fe<sub>2</sub>O<sub>3</sub> supported on nanosheets of graphene shows high anode activity (1355 and 982 mAh/g for charge and discharge cycles, respectively), arising from the redox reactivity at the iron center. However, one serious problem involved in these redox active systems is that upon cycling they tend to drop in performance owing to some irreversible reactions between the Li and the substrate. At higher current densities such undesirable irreversible reactions become more frequent and are typically characterized by their low columbic efficiency. Other carbonaceous support stabilized iron based anodes are also plagued by similar issues. So relatively less reactive (Lewis basic/acidic) and neutral systems could be advantageous when it comes to obtaining prolonged cycle life.

**[0009]** Covalent Organic Nanosheets (CONs) have tunable modular structure and high surface areas. Covalent organic frameworks under hydro/solvothermal conditions can grow into self-exfoliated nanosheets. Their graphene/graphite resembling micro-texture/nano-structure makes them suitable for electrochemical applications. The covalent organic nanosheet (CONs) is a disordered derivative of a COF, and this brings some advantages. While the highly ordered porous structure of a COF could bring advantage kinetics, confinement and accessibility; converting them into relatively more disordered nanosheets could be profitable for a different reason. The disordered carbon nanostructures can in many cases display practical capacities higher than even the theoretical capacity of graphite. Partly this is due to their